1

ALUMINUM ALLOY TUBE AND FIN ASSEMBLY FOR HEAT EXCHANGERS HAVING IMPROVED CORROSION RESISTANCE AFTER BRAZING

Technical Field

5   This invention relates to extruded aluminum alloy products of improved corrosion resistance. It particularly relates to extruded tubes for heat exchangers having improved corrosion resistance after brazing when paired with a compatible finstock.

10   ## Background Art

Commercially produced aluminum microport tubing for use in brazed applications is generally produced in the following manner. The extrusion ingot is cast and optionally homogenized by heating the metal to an

15   elevated temperature and then cooling in a controlled manner. The ingot is then reheated and extruded into microport tubing. This is generally thermally sprayed with zinc before quenching, drying and coiling. The coils are then unwound, straightened and cut to length.

20   The tubes obtained are then stacked with corrugated fins clad with filler metal between each tube and the ends are then inserted into headers. The assemblies are then banded, fluxed and dried.

The assemblies can be exposed to a braze cycle in

25   batch or tunnel furnaces. Generally, most condensers are produced in tunnel furnaces. The assemblies are placed on conveyor belts or in trays that progress through the various sections of the furnace until they reach the brazing zone. Brazing is carried out in a

30   nitrogen atmosphere. The heating rate of the

assemblies depends on the size and mass of the unit but the heating rate is usually close to 20°C/min. The time and temperature of the brazing cycle depends on the part configuration but is usually carried out

5   between 595 and 610°C for 1 to 30 minutes.

A difficulty with the use of aluminum alloy products in corrosive environments, such as automotive heat exchanger tubing, is pitting corrosion. Once small pits start to form, corrosion actively

10   concentrates in the region of the pits, so that perforation and failure of the alloy occurs much more rapidly than it would if the corrosion were more general. With such a large cathode/anode area ratio, the dissolution rate at the active sites is very rapid

15   and tubes manufactured from conventional alloys can perforate rapidly, for example in 2-6 days in the SWAAT test.

Zinc coating applied to the tube after extrusion acts to inhibit corrosion of the tube itself. However

20   during the braze cycle, the Zn layer on the extruded tube starts to melt at around 450°C and once molten, is drawn into the fillet/tube joint through capillary action. This occurs before the Al-Si cladding (fin material) melts at approximately 570°C and as result

25   the tube-to-fin fillet becomes enriched with Zn, rendering it electrochemically sacrificial to the surrounding fin and tube material. A problem with thermally spraying with zinc before brazing is therefore that the braze fillets become zinc enriched

30   and tend to be the first parts of the units to corrode. As a result, the fins become detached from the tubes,

reducing the thermal efficiency of the heat exchanger. In addition to these physical effects, any enrichment of the fillet region with Zn has the effect of reducing the thermal conductivity of the prime heat transfer

5   interface between the tube/fin. There is also a desire to move away from the use of zinc for cost savings and for workplace environment reasons.

In an assembly of brazed tubes and fins, it has been found to be advantageous to have the fins corrode

10   first and thereby galvanically protect the tubes. Most fin alloys used with extruded tubes are clad alloys where the core alloys are either 3XXX or 7XXX series alloy based and contain some zinc to make them electronegative, and thereby provide this type of

15   protection. By making the fin sufficiently electronegative, the tubes to which the fins are brazed can be protected, in this way, if the zinc content of the fin is raised sufficiently. However, this has a negative impact on the thermal conductivity of the fin

20   and on the ultimate recyclability of the unit. Furthermore, if the fin material is too electronegative it can corrode too fast and thereby compromises the thermal performance of the entire heat exchanger. Corrosion potential and the difference between

25   corrosion potential of tube and fin have been frequently used to select tube and fin alloys to be galvanically compatible (so that the fin corrodes before the tube). This technique serves to give an approximate galvanic ranking. In order to obtain a

30   true determination of the performance of such combinations it has been found that a measurement of the direction and magnitude of the galvanic current

permits a better determination of ultimate performance.
Little attempt has been made to optimize the tube-fin
combination in heat exchangers based on extruded tubes
through the use of appropriate alloys alone, the use of
5 zinc cladding being widely used instead. One
constraint on such optimization is that it still also
must be possible to extrude the tubes without
difficulty.

Anthony et al., U.S. Patent 3,878,871, issued
10 April 22, 1975, describes a corrosion resistant
aluminum alloy composite material comprising an
aluminum alloy core containing from 0.1 to 0.8%
manganese and from 0.05 to 0.5% silicon, and a layer of
cladding material which is an aluminum alloy containing
15 0.8 to 1.2% manganese and 0.1 to 0.4% zinc.

Sircar, U.S. Patent 5,785,776, issued July
28,1998, describes a corrosion resistant AA3000 series
aluminum alloy containing controlled amounts of copper,
zinc and titanium. It has a titanium content of 0.03
20 to 0.30%, but this level of titanium raises the
pressures required for extrusion, which will ultimately
lower productivity.

In Jeffrey et al., U.S. Patent 6,284,386, issued
September 4, 2001, extruded aluminum alloy products
25 having a high resistance to pitting corrosion are
described in which the alloy contains about 0.001 to
0.3% zinc and about 0.001 to 0.03% titanium. The
alloys preferably also contain about 0.001 to 0.5%
manganese and about 0.03 to 0.4% silicon. These
30 extruded products are particularly useful in the form
of extruded tubes for mechanically assembled heat
exchangers.

It is an object of the present invention to provide brazed extruded aluminum alloy tubing for heat exchangers having adequate corrosion resistance without special treatments, such as thermal spraying of the surface with zinc, and also being galvanically compatible with fins joined thereto.

It is a further object of the present invention to provide a brazed heat exchanger assembly consisting of extruded tubing and fins in which the tubing alloy is optimized to minimize self corrosion and so that the heat exchanger is protected from overall corrosion by a slow corrosion of the fins.

Disclosure of the Invention

The present invention in one embodiment relates to an aluminum alloy for an extruded heat exchanger tube comprising 0.4 to 1.1% by weight manganese, preferably 0.6 to 1.1% by weight manganese, up to 0.01% by weight copper, up to 0.05% by weight zinc, up to 0.2% by weight iron, up to 0.2% by weight silicon, up to 0.01% by weight nickel, up to 0.05% by weight titanium and the balance aluminum and incidental impurities.

Further embodiments comprise an extruded tube made from the above alloy and such a tube when brazed.

In a yet further embodiment, the invention relates to a brazed heat exchanger comprising joined heat exchanger tubes and heat exchanger fins, where the tubes are extruded tubes made from a first alloy comprising the aluminum alloy described above and the fins are formed from a second alloy comprising an aluminum alloy containing about 0.9 to 1.5% by weight Mn and at least 0.5% by weight Zn, or an aluminum alloy

6

of the AA3003 type, with this second alloy further
containing at least 0.5% by weight zinc.

   Fin alloys of this type have sufficient mechanical
properties to meet the heat exchanger construction
5 requirements.

   It appears that the above unique combination of
alloying elements for the tubes gives unexpectedly good
self anti-corrosion results for the tubes without the
need for any coating of zinc. Also by keeping the
10 manganese content of the tube alloy within 0.8% by
weight of that of the fin or greater than or equal to
the manganese content in the fin, the fin remains
sacrificial, thus protecting the tube and the galvanic
corrosion current remains relatively low so that the
15 fin is not corroded so rapidly in service that the
thermal performance of the assembly is compromised.

   The above combination of aluminum alloy fins and
extruded tubes when assembled and furnace brazed
exhibit a very slow and uniform corrosion of exposed
20 fin surfaces, rather than localized pitting of the
tube. The invention is particularly useful when the
tubes are microport tubes and the assembly has been
furnace brazed in an inert atmosphere.

   When a brazed heat exchanger is manufactured with
25 these alloy limitations, the heat exchanger tubes can
be used without a zincating treatment. The heat
exchanger tube does not show self-corrosion in areas
remote from the fins (e.g. in between the header and
fin pack), and the fins corrode before the tubing but
30 at a rate sufficiently slow to ensure performance of
the heat exchanger is maintained for extended periods
of time.

Brief Description of the Drawings

        The present invention will be described in
conjunction with the following figures:

        Fig. 1 is a micrograph of a section of a brazed
fin and tube assembly of a fin and tube combination
outside the scope of this invention.

        Fig. 2 is a micrograph of a section of a brazed
fin and tube assembly of a further fin and tube
combination outside the scope of this invention.

        Fig. 3 is a micrograph of a section of a brazed
fin and tube assembly of a fin and tube combination
within the scope of this invention.

        Fig. 4 is a graph of corrosion potential as a
function of manganese content of various extruded tubes
and fin materials showing the relationship between
manganese content and corrosion behaviour.

Best Modes for Carrying Out the Invention

        According to a preferred feature, the fin alloy
has less than about 0.05% by weight of copper to make
it galvanically compatible with the amount of copper in
the extruded tube.

        Manganese in the tube alloy in the amount
specified provides for good self-corrosion protection,
along with adequate mechanical strength yet still
permits the tubing to be easily extruded. If the
manganese is less than 0.4% by weight the tube itself
can corrode when coupled with the fin, and if greater
than 1.1% by weight the extrudability of the material
is adversely affected. When the manganese levels in

the tube alloy is less than the manganese in the fin
alloy by less than 0.8% by weight (and preferably by
less than 0.6% by weight), or is greater than the
manganese in the fin alloy, then the fin remains
sacrificial to the tube, the corrosion current remains
low and therefore the rate of fin corrosion is
acceptable. To meet compatibility requirements under a
broad range of conditions, it is preferred that the
manganese level in the tube therefore be greater than
0.6% by weight. The conditions on manganese can be
expressed as a formula,

$Mn_{tube} > Mn_{fin} - 0.8$, provided that Mn_{tube} is in the
range 0.4 to 1.1 wt%

or more preferably

$Mn_{tube} > Mn_{fin} - 0.6$, provided that Mn_{tube} is in the
range 0.4 to 1.1 wt%

A particularly preferred tube alloy composition
contains 0.9 to 1.1% by weight of manganese, since this
represents an alloy that can be extruded into the
desired tubes whilst minimizing the manganese
concentration differences between tube and fin.

The fin also remains sacrificial to the tube if
the manganese content is greater than or equal to that
of the tube, but because many commercial fin alloys
have Mn levels of about 1%, tube alloys having
manganese greater than 1% are less generally useful in
the present invention because of increased difficulty
in extrudability.

The relative manganese content of the fin and tube
alloys can also be expressed by the measured galvanic
corrosion current. The measured galvanic corrosion
current from the fin to the tube must preferably exceed

9

+0.05 microamps per square centimeter when measured via ASTM G71-81.

The zinc content of the tube must be maintained at a low level to ensure that the fin remains sacrificial
5   to the tube. Even relatively low levels of zinc can alter the galvanic corrosion current and thereby alter this sacrificial relationship. The zinc must therefore be kept at less than 0.05% by weight, more preferably at less than 0.03% by weight.

10   Iron, silicon, copper and nickel all contribute to self-corrosion of the tube and therefore must be below the stated levels. In addition, iron above 0.2% by weight results in poor extrusion surface quality.

Titanium additions to the alloy make it difficult
15   to extrude and therefore the titanium should be less than 0.05% by weight.

The alloy billets are preferably homogenized between 580 and 620°C before extrusion into tubes.

Example 1:
20   Tests were conducted using the alloys listed in Table 1 below:

Table 1

Alloy	Cu	Fe	Mg	Mn	Ni	Si	Ti	Zn
A	<.001	0.09	<.001	0.22	<.001	0.058	0.017	0.004
B	0.014	0.07	<.001	0.23	<.001	0.07	0.008	0.17
C	0.015	0.51	0.021	0.33	0.001	0.32	0.014	0.007
D	0.001	0.08	<.001	0.98	0.002	0.064	0.014	0.18
E	0.015	0.09	<.001	1.00	<.001	0.07	0.007	0.18
F	<.001	0.08	<.001	0.98	0.001	0.071	0.008	0.005
G	0.006	0.11	0.001	0.42	0.001	0.078	0.023	0.027
H	0.006	0.10	0.002	0.63	0.001	0.079	0.021	0.029
I	0.001	0.09	<0.001	0.61	0.002	0.08	0.016	0.002
J	0.0035	0.11	<0.001	0.62	0.002	0.09	0.016	0.002
K	0.08	0.59	<0.001	1.05	<0.001	0.23	0.01	0.01

These alloys were cast into 152 mm diameter billets. Alloy C was a commercial 3102 alloy and Alloy K a commercial 3003 alloy. The billets were further machined down to 97 mm in diameter and homogenized

5 between 580 and 620°C. They were then extruded into tubes. Samples of the tubing were subjected to a simulated brazing process and then subjected to a SWAAT test using ASTM standard G85 Annex 3 and galvanic corrosion currents were measured against a standard

10 finstock material manufactured from AA3003 alloy containing 1.5% by weight added zinc and clad with AA4043 alloy that had also been given a simulated braze cycle, in accordance with ASTM G71-81. The results are shown in Table 2 below:

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Table 2

Alloy	SWAAT life (days)	Galvanic corrosion current (μA/cm^2) *
A	56	-3.2
B	<20	
D	56	-2.4
E	<20	
F	56	0.2
G	55	3.1
H	55	5
I	55	
J	55	
F unhomogenized	21	
C zincated	56	-26.9
K	< 5	

* +ve corrosion current = current flow from fin to tube
  -ve corrosion current = current flow from tube to fin

The results of a test carried out on a zincated 3102 tube (e.g. Alloy C, Extruded and zincated) are

shown for comparison. In Table 2, a SWAAT life of 55
to 56 days indicated no perforation of the tube by
self-corrosion and a positive galvanic corrosion
current indicates that the fin corrodes preferentially.

5   A small value indicates a low rate of corrosion. A
sample of alloy F was also extruded without
homogenization and subjected to a SWAAT test.

Alloys A, D have compositions outside the claimed
range. They nevertheless show excellent SWAAT

10   performance indicating that for self-corrosion these
alloys would be also be acceptable even when the Mn is
less than the range of this invention. It is believed
that this is a result of the low Cu, Fe and Ni in these
alloys. The amount of Mn present has no significant

15   effect on the self-corrosion behaviour. However, the
galvanic corrosion current is unacceptable for these
compositions. This is believed to be due to manganese
levels that are too low in one case and zinc levels
that are too high in the other. Both these elements

20   are important in ensuring acceptable performance of the
fin-tube galvanic couple.

Samples of extruded heat exchanger tubing made
from alloys A, D and F were brazed into heat exchanger
assemblies using fins manufactured from AA3003 with

25   1.5% Zn. The AA3003 composition had 1.1% by weight Mn.
The assemblies were then exposed to SWAAT testing and
examined metallographically. The results are shown in
Figures 1 to 3. Figures 1 and 2, correspond to alloys
A and D tubing incorporated into a heat exchanger after

30   8 and 7 days exposure respectively to the SWAAT test.
Substantial pitting corrosion of the tubes near the fin
is observed, although in tests of the tube alone, no

pitting occurred after long exposure. Figure shows a
combination of tubing of Alloy F with the same fin
stock (i.e. a combination within the scope of this
invention), in which there was no through-thickness
5   pitting until after 20 days SWAAT exposure (compared to
7 or 8 days for the combinations outside the scope of
the invention). A 20 day life is considered under this
test to be adequate performance.

Alloys B, E and K have copper outside the desired
10   range and show poor SWAAT results, indicating that
alloys with such a copper level would suffer from
excessive self-corrosion, whether or not the manganese
composition met the requirements. Alloy D has a zinc
level that exceeds the desired range and shows that
15   although the manganese level is within the desired
range, the fin-tube galvanic corrosion current is
negative and the tube would therefore corrode first.
The self-corrosion performance (SWAAT test) is
acceptable, but because of the fin-tube galvanic
20   corrosion, the overall assembly would fail. Alloy K
also has Fe and Si above the required amounts.

Alloys F, G, I and J lie within the claimed range.
Alloys F, G and H exhibits acceptable performance on
both the SWAAT tests on the tubing and the galvanic
25   corrosion behaviour. Alloys I and J show good SWAAT
behaviour, and lack any significant levels of elements
that would give poor galvanic current performance.

Alloy F in un-homogenized condition however, shows
unacceptable SWAAT performance indicating that
30   homogenization of the product is a preferred process
step to achieve good performance.

13

Finally Alloy C was a standard tube alloy and was tested in zinc-coated form. As expected this gave good SWAAT performance, since the zinc layer is sacrificial to the entire tube and so overcomes the negative

5   effects of elements such as copper. The negative galvanic corrosion current in this case indicates that the zinc surface layer is sacrificial as noted above. Alloy C had manganese less than the desired range and only performs because of the presence of the zinc

10   coating. However, as noted above, zinc has a number of negative features that mean it is not used in the present invention.

Example 2:

In order to show the effect of changes in fin Mn

15   composition, the corrosion potential of the various tube alloys of Example 1 were compared to the corrosion potential of various fin alloys. A necessary condition for the fin to be sacrificial with respect to the tube is that the tube corrosion potential be clearly less

20   negative than the fin corrosion potential. The corrosion potential of the tube alloys of Example 1 were determined and plotted on a graph in Figure 4 showing the variation with manganese content. Curves are shown for the tube alloys in the as-cast condition

25   as well as following homogenization at 580 or 620°C.

Various fin alloys (identified as samples 1 to 3) based on the commercial AA3003 with 1.5% Zn composition, but having different Mn compositions within the preferred Mn range of the present invention, were prepared by

30   book mould casting, processed to finstock gauge by hot

and cold rolling. They were then subjected to a
simulated braze cycle and the corrosion potential
measured. The compositions and measured corrosion
potentials are given in Table 3.

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Table 3

Sample No	Cu	Fe	Mg	Mn	Ni	Si	Ti	Zn	E_{corr} (mV)
1	0.12	0.53	0.010	1.08	0.004	0.29	0.011	1.50	-790
2	0.133	0.55	0.0003	0.9	0.002	0.34	0.007	1.61	-797
3	0.13	0.55	0.0004	1.24	0.002	0.33	0.006	1.63	-786

The corrosion potentials for samples 1 to 3 are shown
as horizontal dashed lines on Figure 4. In order that
the fin material be sacrificial compared to the tube
alloy the fin corrosion potential must be more negative

10 that the tube alloy corrosion potential. For practical
reasons and to account for inevitable variation in
materials, only tube alloy compositions that have
corrosion potentials that exceed (are less negative
than) those of the fin by 25 mV are selected. From

15 Figure 4, therefore, the minimum tube manganese level
compatible with each of the three fin manganese
compositions is determined. These are given in Table
4, along with the corresponding tube manganese
composition and the minimum acceptable tube manganese

20 in accordance with the formula:

$Mn_{tube} > Mn_{fin} - 0.8$ wt% except $0.4 <= Mn_{tube} <= 1.1$ wt%

Table 4

Fin sample	Mn in fin	Measured minimum acceptable Mn in tube	Calculated minimum acceptable Mn in tube
1	1.08	0.43	0.40
2	0.9	0.40	0.40
3	1.24	0.48	0.44